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Microwave Assisted Synthesis, Characterization of Flower Like ZnO/TiO_2 Nano Composites for the Removal of Congo Red Dye

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Abstract

In this work we synthesized flower likeZnO/TiO_2 nanocomposite by chemical precipitation method using microwave irradiation. The ZnO nanoparticle was decorated by TiO_2 nanoparticle. The structure and morphology of the resulting particles were characterized by XRD, SEM, EDAX, TEM, FT-IR & UV-Visible analysis. The X-ray analysis confirms the co-existence of anatase and rutile TiO_2 phases with hexagonal wurzite ZnO phase. The scanning electron microscopy reveals that the TiO_2 located on the surface of the ZnO flowers. The similarities in photo degradation mechanism, ZnO and TiO_2 have comparable band gap energy, and have very good reputation as photo catalysts. The nanoparticles have large surface area and thus provide a large number of active sites for interaction among the particles of different oxides. To achieve, ZnO/TiO_2 nanocomposite having particle size, strictly, in the nano domain, was synthesised. The as prepared flower like ZnO/TiO_2 sample showed excellent photocatalytic activity for the degradation of Congo red under direct exposure to sun light.

Keywords: *Congo red; Nanocomposite; Microwave irradiation; Photocatalyst.*

1. INTRODUCTION

In recent years, semiconductor photocatalysis has attracted a great deal of research attention due to its potential application to solve environmental problems (Dimitrijevic *et al.* 2005; Rabatic *et al.* 2006).Since a photocatalytic process is based on the generation of electron/hole pairs by means of band-gap radiation, the coupling of different semiconductor oxides seems useful to achieve a more efficient electron/hole pair separation under irradiation and a higher photocatalytic activity (Yoon *et al.* 1999). Metal oxide nanoparticles attract great attention in recent years an account of their special electronic and chemical properties (Stoyanova *et al.* 2013). TiO_2 is largely used as photocatalyst due to its high photocatalytic efficiency, physical and chemical stability,low cost and toxicity.Recently several papers concerning the enhancing of TiO_2 photocatalytic activity have been reported (Diamandeseu *et al.* 2008; Tong *et al.* 2008). Most of them concern modifying the photo catalyst by coupling TiO_2 to other oxides. ZnO can be used as a photocatalyst and has drawn increasing attention because its photocatalytic activity is comparable to that of TiO_2 (Duan *et al.* 2010; Zhang *et al.* 2010). Hierarchical ZnO with flower like morphology shows promising application in decomposition of organic pollutant due to the increased optical absorption efficiency and large specific surface area (Xu *et al.* 2010; Zhou *et al.* 2008). Coupled semiconductor photo catalyst of TiO_2/ZnO has also been investigated to enhance the photo degradation efficiency of TiO_2 catalyst by a number of researchers and its effect for improving photo catalytic efficiency was reported (Liao *et al.* 2008; Wang *et al.* 2009; Xu *et al.* 2011; Janitabar-Darzi *et al.* 2009).Zinc oxide has achieved applications in various areas such as optical, magnetic and gas sensing properties and apart from this, zinc compounds have been generally regarded as safe (Wahab *et al.* 2010). In this paper, flower like ZnO/TiO_2 composites were fabricated through a chemical co-precipitation process. The as prepared composite including TiO_2 particles deposited on the petal surfaces of ZnO flowers shows high crystallization.

Last few decades numerous research effect in the field of photocatalysis by semiconducting materials through particular system has been studied (Neeri, 1988; Kanan *et al.* 2001). Textile dye produces huge amount of polluted effluents that are normally discharged on the surface water bodies and ground water aquifers(Muhammedjaved Iqbal *et al.* 2007). This waste water causes damages to the ecological system of the receiving surface water capacity and certain a lot of disturbance to the ground water resources. Most of the dyes used in the textile industries are stable to light and biodegradable (Dave *et al.* 2010). In order to reduce the risk of environmental pollution from such as waste water, it is necessary it treat them before discharging it into the environment (Biswa Mohan

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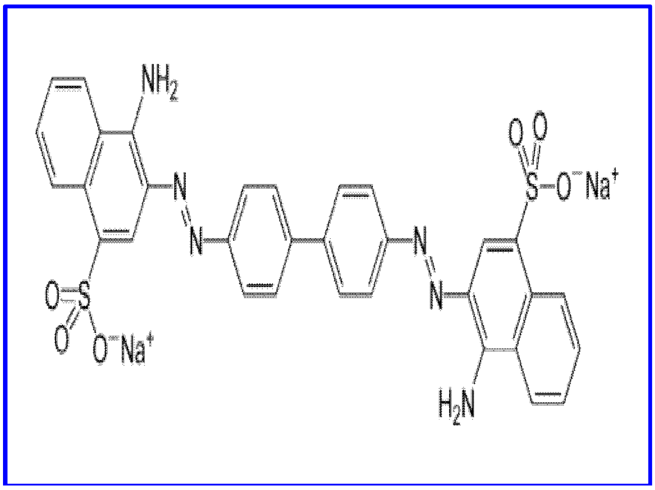
Sahov *et al.* 2013). However the aqueous phase photochemical degradation of Congo red has been studied in the presence of semiconducting oxides like flower like ZnO/TiO_2. There are several methods of nano particles synthesis such as sol-gel, organometallic, hydrothermal and microwave methods. In the present study, flower like ZnO/TiO_2 nanocomposites were prepared by using microwave irradiation. Due to the intense friction and the collision of molecules created by microwave irradiation, microwave irradiation not only provides the energy for heating but also accelerates the nucleation. With microwave irradiation on the reactant solution, temperature and concentration gradients can be avoided leading to uniform nucleation.Microwave-based synthesis method is one of the easiest, energy-saving, green and quick methods for large scaleproduction of nanomaterials.Microwave synthesis is the novel route of synthesis of metal oxide semiconductor nano particles which is clean, cost-effective, energy-efficient, eco-friendly, rapid and convenient method of heating and results in higher yields in shorter reaction times (Singh *et al.* 2013).



Structure of Congo red dye

The structure and morphology of the resulting particles were characterized by XRD, SEM, TEM, FTIR & UV-Visible analysis. The photocatalytic activities of these nanoparticles were studied for Congo red dye under sunlight.

2. EXPERIMENTAL

2.1 Materials

The chemicals used in this study were of analytical grade purity and were procured from Merck chemical reagent company, India.

2.2 Preparation of ZnO/TiO_2 nano composite

2.2.1 Preparation ofZnO

All the chemicals used for the synthesis of flower like ZnO are analytical grade reagents. ZnO nanostructure was synthesised by a simple wet chemical route using precipitation from aqueous solutions of zinc acetate dihydrate and KOH. In a typical synthesis, calculated amount of zinc acetate dihydrate was added into 100 ml of doubly distilled water under stirring to prepare 0.02 M solution. KOH was added directly into the above solution at 60 ^{o}C under stirring to reach concentrations 10 times higher than the corresponding Zn^{2+} concentration. The stirring was continued for 3hrs with the temperature being maintained at 60 ^{o}C. Subsequently, the solution was allowed to cool down and left undisturbed overnight. The white precipitates formed were centrifuged and thoroughly washed by repeated centrifugation-dispersion cycles with doubly distilled water. After this,the precipitates were dried overnight in an oven at 80 ^{o}C, solid white powder was obtained (Sini Kuriakose *et al.* 2013).

2.2.2 Preparation ofTiO_2 nanoparticles

For the preparation of TiO_2,ethanol and HCl was stirred for half an hour in a magnetic stirrer, titaniumtetraisopropoxide and isopropanol was added slowly with constant stirring for 30 minutes. Hydrolysis of titaniumtetraisopropoxide done by adding distilled water slowly with continues stirring.The mixture was refluxed under vigorous stirring at 70 ^{o}C for 1hr as titania sol was prepared (Balachandran *et al.* 2010).

2.2.3 Preparation of ZnO/TiO_2 nano composite

Flower-like ZnO/TiO_2 composites was prepared by chemical precipitation method. A typical experimental process for the composite with a mole ratio of 1:1 is given as follows:4 g of flower-like ZnO was dispersed in 100 mL deionised water and isopropanol was added to the mixture in order to immerse ZnO thoroughly. Simultaneously, titaniumtetraisopropoxide and isopropanol was added to the ethanol / HCl mixture then added to the above suspension and stirred magnetically for 30 minutes. The resulting white aqueous solution, which was then transferred into Teflon-line stainless steel autoclave. The autoclave was introduced in microwave irradiation system. The reaction products in the form of a precipitate were filtered and washed with distilled water and ethanol to remove the ions possibly remaining in the final products. Finally the products were dried in hot air oven at 80^{o}C. The final white productwas collected for characterization. In this process the heating microwave radiation interacts with the polar molecules possessing dipole moment and makes them reorient through rotation. A large number of molecules try to orient together resulting in collision and production of heat. Thus microwave heating is energy conservation method in which electromagnetic radiation is converted into heat energy rather than heat transfer by convection in conventional heating.

The average crystalline size and morphology of the prepared flower-like ZnO/TiO_2 nano composite was determined from XRD pattern. These materials are used for photocatalysis for removal of Congoreddye from aqueous solutions.

2.3 Characterization

The optical property of the synthesized ZnO/TiO_2 nanocomposite was analysed using UV-Vis spectrophotometer (Carry 5000, Varian, USA). The crystalline structure was examined using D8 Advance X-ray diffraction (Bruker AXS, Germany) at room temperature, operating at 30 kV and 30 mA, using CuKα radiation (λ = 0.15406 nm) and crystal size was calculated by Scherer's formula. Morphology was determined by scanning electron microscope (SEM) (Model JSM 6390LV, JOEL, USA), EDX and functional groups were characterized by Fourier transform infrared spectroscopy (FTIR) spectra (Bruker, Germany) with a wave number range of 4000 to 400 cm^{-1}. The size and size distribution were determined by transmission electron microscopy (TEM) (JEOL JEM-3100F) (Muhammed Javed Iqbal *et al.* 2007).

2.4 Photo catalytic activity experiments

Experiments were performed with aqueous solution of Congo red with flower- like ZnO/TiO_2 nanocomposite under sunlight irradiation. Flower-like ZnO/TiO_2-Congored suspensions were prepared for 20-40 to 100 mgL^{-1} of Congo red. Prior to sunlight radiation (2h irradiation) the suspension were stirred for 15 min. 10 mL of the sample was collected and centrifuged to remove nanoparticles and the clear solution was carefully transferred into a quartz cuvette and the absorption was evaluate by UV-Vis spectrometer (λ_{max}). The dye decomposed after equilibrium time was separated by centrifugation and the quantity of dye decomposed was determined by employing a UV-Visible spectrometer, in respective λ_{max} 497 nm of the dye. The percentage of dye removal was calculated from the absorbance value before and after treatment. The Photocatalytic degradation efficiency of the dye solution was calculated using the following equation,

$$R(\%) = ((A_0 - A)/A_0) \times 100$$

where A_0 is the absorbance of dye solution before the illumination, A is the absorbance of dye solution after degradation (Lingling Xu *et al.* 2013).

3. RESULTS & DISCUSSION

3.1 UV-Visible absorption spectroscopy

UV-Vis absorption spectra of ZnO/TiO_2 nano composite shown in fig.1. A higher absorbance observed at 336 nm and absorbance below 336 nm ensures that the TiO_2 nanoparticles, which are attached to ZnO nanoparticles, dominate the deep UV absorption (Chun Cheng). The peak at about 260 nm can be attributed to the charge transfer absorption process involving an electron transfer from O^{2-} to Ti^{4+} ions of the highly dispersed tetrahedral coordinated TiO_4 unit of these catalysts (Gao *et al.* 2003; Calleja *et al.* 2004; Kalita *et al.* 2008; Kim *et al.* 2001). The peaks at the visible range of the spectra above 400nm indicate the ZnO/TiO_2 nano composite.

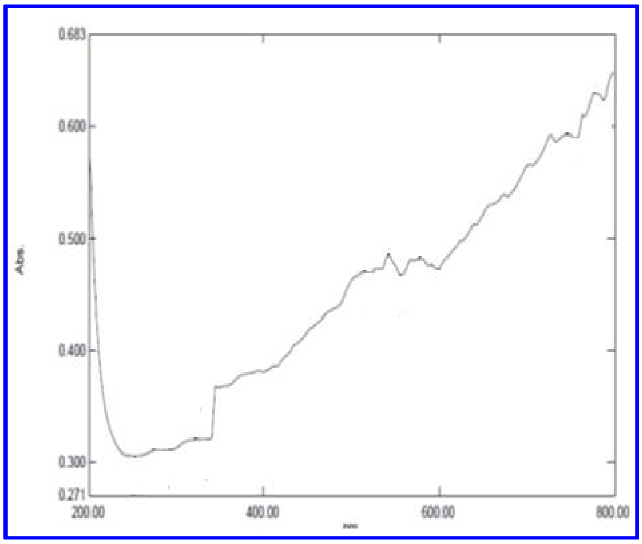


Fig. 1: UV spectrum of ZnO/TiO_2 nano composite

3.2 FT-IR Spectroscopy

FT-IR spectra of samples have been presented in fig. 2 in the wave number range from 400 to 4000 cm−1. The IR spectrum gives a broad peaks at 3346 cm^{-1} corresponding to the O−H stretching vibration (Mali *et al.* 2012). Peaks observed in the range of 1700−1500 cm^{-1} are due to the bending vibrations of adsorbed H_2O and OH group (Yu *et al.* 2001). The peak at 470 cm^{-1} in the IR spectrum was due to the Zn−O vibration (Gegova *et al.* 2013). While the peak at 624 cm^{-1} could be due to the Ti−O vibration (Mali *et al.* 2012). The peaks around 650 and 800 cm^{-1} can be devoted to symmetric stretching vibration of the Ti-O-Ti and vibration mode of Zn-O-Ti groups (Tian *et al.* 2009; Karthik *et al.* 2010; Wang *et al.* 2010).

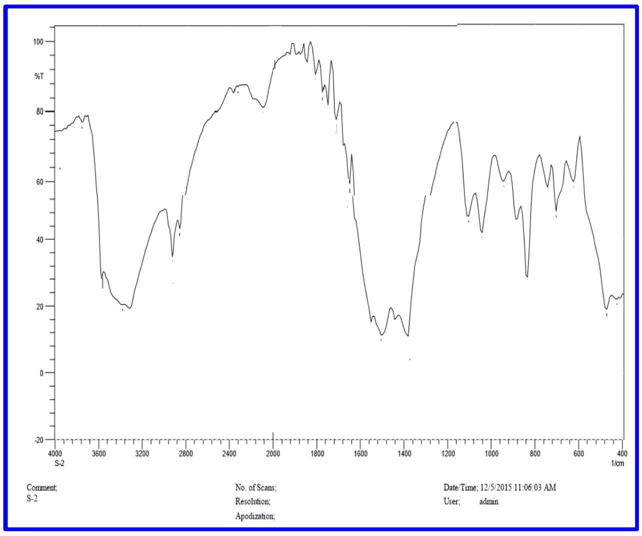


Fig. 2: FT-IR Spectrum of Flower like ZnO/TiO_2 nanocomposite

3.3 XRD Analysis

The X-ray diffraction spectrum of ZnO/TiO_2 nanocomposite was shown in fig.3. The crystalline size (D) of nanoparticles has been calculated by XRD line

broadening of the most intense peak using the Scherrer's formula (Balachandran *et al.* 2010)

$$D= K \lambda / \beta \cos\theta$$

where λ is the wavelength of X-ray, β is the full width and half maxima, θ is Bragg's angle, K is the shape factor. The dimensionless shape factor has a typical value of about 0.9. But varies with the actual shape of the crystallite. Here,K is taken as 0.9. Fig.3 shows the XRD patterns of the TiO_2 coated ZnO nano flower petals indicating the anatase TiO2, Rutile TiO_2 and wurzite ZnO. After TiO_2 coating, on ZnO the XRD pattern had some significant changes and characteristic peaks for anatase and rutile TiO2 crystalline were observed. The peaks at $2\theta = 27^0$, 41^0 and $2\theta = 54^0$, 63^0 corresponds to rutile and anatase phases of TiO_2 respectively and the peaks at 2θ=35.830, 56.30, 68.90 indicates (101), (110), (201) which were related to zinc phases, respectively (Ahsan Habib *et al.* 2013). The intense and sharp diffraction peaks shown that the content of TiO_2 is much more than that of ZnO (Lingling Xu *et al.* 2013).The Crystallite size of flower like ZnO/TiO_2 nanocomposite, calculated from the most intense peak was about 85 nm.

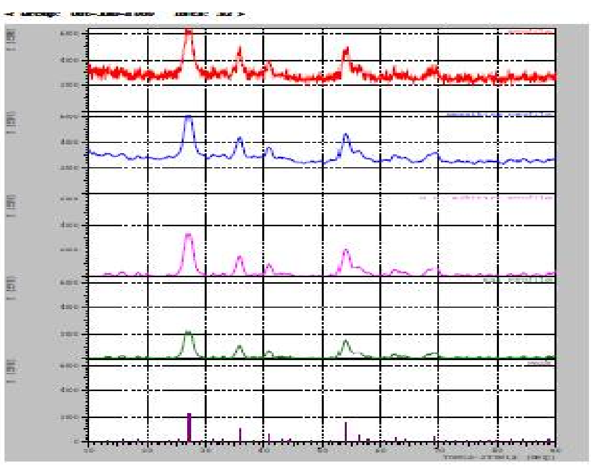


Fig. 3: XRD of Flower like ZnO/TiO_2 nanocomposite

3.4 Morphology and Elemental Analysis

In order to obtain the detail information about the morphology of the synthesised ZnO/TiO_2 nanocomposite the SEM analysis was carried out and the results were shown in fig.4. The SEM image reveals that ZnO possesses the flower like rough surface with petals and ZnO/TiO_2 nanocomposite had a uniformly dispersed morphology, without any agglomeration was observed. The rough surfaces of ZnO provide a very good platform to locate TiO_2 nanoparticles which are present on the petals. The SEM image shows the particles are of nearly uniform size in the Nano domain. The driving force for the heterogeneous bonding between the ZnO and TiO_2 particles was Coulombic attraction which is interdependent of the respective surface charge of each component (Lingling Xu *et al.* 2013). Fig.5 demonstrates the EDS analysis of ZnO/TiO_2 nanocomposite. This proves that Zn was incorporated into the TiO_2 nanoparticles to form nanocomposite (Janitabar-Darzi *et al.* 2009; Kanan *et al.* 2001).

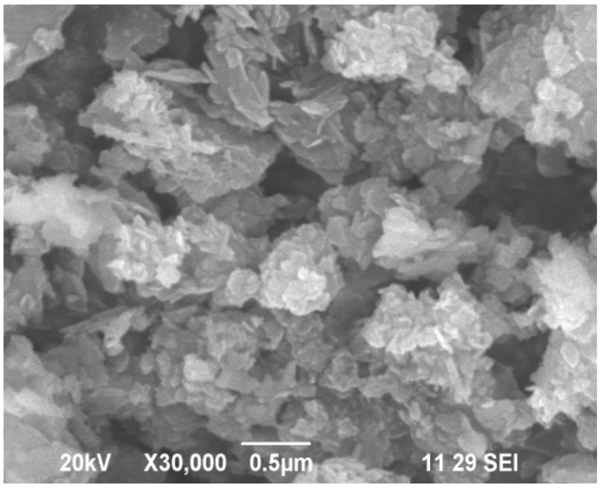


Fig. 4: SEM Analysis of flower like ZnO/TiO_2 nanocomposite

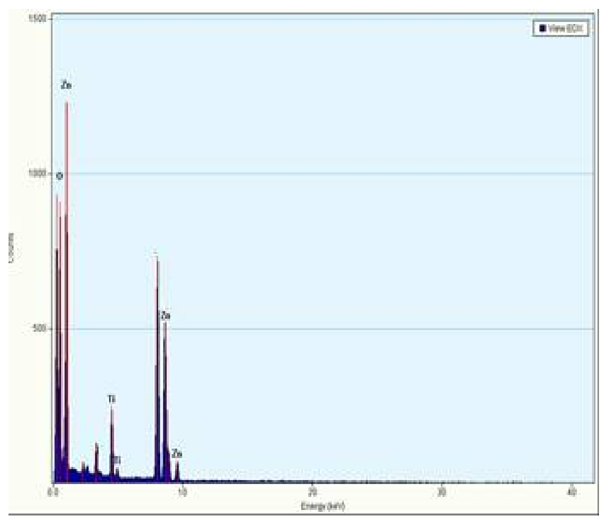


Fig. 5: EDAX of Flower like ZnO/TiO_2 nanocomposite

3.5 TEM Analysis

The transmission electron micrographs (TEM) of the composites are shown in fig 6. The Figure clearly refers the morphology of the composites to be almost uniformly deposited in nature and few are bigger. These last ones would be responsible for the dispersion effect that is observed as a mild decline of the signal towards longer wavelengths in the UV-Vis extinction spectra (Virginia Roldán *et al.* 2013). It is observed that the lighter TiO_2 shell is present on the darker ZnO petals. It can be seen from TEM image that the ZnO/TiO_2 sample consist with the size of 85-100 nm which is approximately in conformity to XRD result.

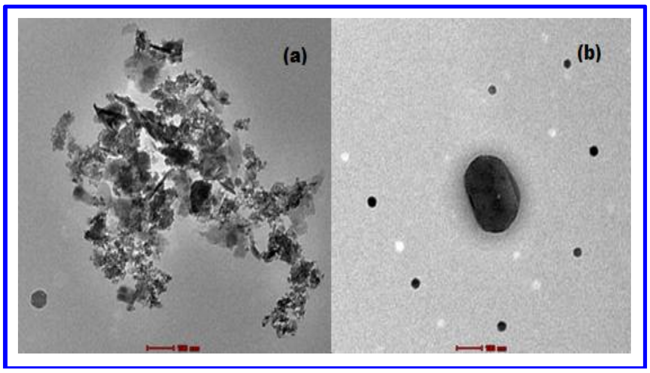


Fig. 6: TEM analysis of Flower like ZnO/TiO_2 nanocomposite

3.6 Photocatalytic activity measurements

The Photocatalytic activity of ZnO/TiO_2 nanocomposite were measured by photo degradation of Congo red by using sunlight as the light source by taking into consideration of various parameters such as contact time, catalyst dosage and p^H. It is to be noted that no significant decolourisation of Congo red under sunlight was observed in the absence of photocatalyst, indicating that the dye was resistant to self-photolysis in aqueous solution under sun light.

3.6.1 Effect of Catalyst Loading

The effect of photocatalyst concentration was analysed to optimize the amount of ZnO/TiO_2 nanocomposite. It can be deduced from the results obtained that the photocatalytic efficiency of ZnO/TiO_2 nanocomposite was shown to be remarkably greater in decolourisation of Congo red dyefrom 0.1g to 0.5g/l. It's clear from Fig.7a that the photocatalytic activity increases with the increase in the concentration ofZnO/TiO_2nanocomposite.

3.6.2 Effect of contact time

The effect of contact time on the removal of Congo red was evaluated for various concentrations of nanocomposite (0.1 to 0.5 g/l) for the treatment of dye ranging from 20 ppm to 100 ppm, at different time period. Fig. 7b depicts an increase in dye removal with increase in time and concentration of the catalyst. The increase in catalyst amount increased the number of active sites on the photocatalyst surface causing increase in the number of •OH radicals which take part in actual decolourisation of dye solution.

3.6.3 Effect of pH

The effect of pH on adsorption percentages of Congo red was investigated over the range of pH values from 2 to 12. The removal efficiency percentage of Congo red was enhanced by increasing pH up to 6 and the reverse performance was observed at about pH of 10. While the removal efficiency percentage of Congo red was enhanced by decreasing pH to acidic solution. At pH 2, the maximum amount catalytic activity is about 100% while by increasing the pH to 12, the removal efficiency can reach 59%. The pH of the solutions thus, seems to affect the rate of reaction on photo catalyst surfaces which is related to the surface charge properties of the semiconductors. The point of zero charge (pzc) for ZnO/TiO_2 is at pH 6. The photo catalyst is positively charged at pH <pzc which favoured adsorption of the negatively charged Congo red due to the interaction of holes or hydroxyl radicals with Congo red. At pH >pzc, the photocatalyst surface become negatively charged and adsorption of CR is not favourable(Hossein Habibi *et al.* 2015).

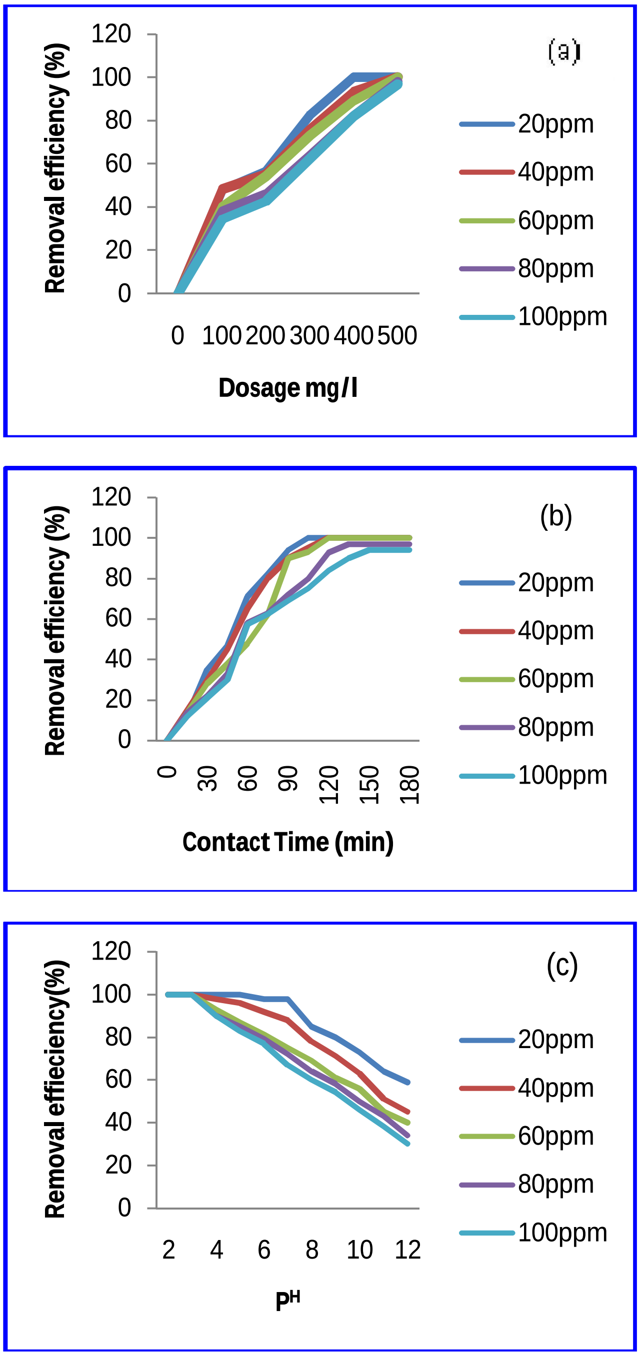


Fig. 7: Effect of (a) contact time and initial dye concentration on Congo red(b) Effect of catalyst loading on Congo red (c) Effect of pH on removal of Congo red

4. CONCLUSION

TiO_2 decorated ZnO nanocomposite was synthesized via chemical precipitation process. The XRD profile confirms that the composite is composed of anatase and rutile TiO_2 with wurtzite ZnO. The morphology of the composite is a TiO_2 decorated on the rough surface of flower-like ZnO, which was proved by SEM analysis and the presence of Ti, Zn and O are shown by EDS-analysis. The flower-like morphology and the fast electron-hole pair recombination in ZnO could be suppressed by coupling with TiO_2, which enhance the photocatalytic efficiency. The pH also effect the rate of decolourisation, by increasing of pH reduces the rate of decomposition of Congo red. It can be concluded that flower like ZnO/TiO_2 is an efficient photo catalyston Congo red decolourisation.

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